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PHOTOCHEMICAL PROCESSES AT THE SOLID-GAS INTERFACE:
THE ADSORPTION AND REACTIONS OF GASEOUS CO₂ AND H₂O ON
Pt-SrTiO₃ SINGLE CRYSTAL SANDWICHES

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Abstract

We have observed the photoassisted production of methane from carbon dioxide and water vapor in contact with a sandwich consisting of single crystal SrTiO$_3$ and platinum foil. In an attempt to elucidate the fundamental chemical processes involved in this reaction, we have studied the chemisorption of H$_2$O, O$_2$, CO, and CO$_2$ on SrTiO$_3$(111) crystals. The mechanism of methane production is discussed in light of the chemisorption results.
Introduction

The purpose of our studies is to carry out thermodynamically uphill chemical reactions, at solid surfaces, with the help of light as the source of energy. This may be carried out two ways: 1) By excitation of the solid by light that creates mobile electrons or electron-hole pairs that may be available to the adsorbates at the surface. By transfer of the excited electrons to or from the adsorbed molecules the surface chemical reactions become energetically feasible; 2) by direct excitation of the adsorbed molecules by light. The stable molecules when placed in an excited electronic or vibrational state may become energetic enough so that their surface reactions are thermodynamically feasible.

One of the simplest reactions of the first type described above is the dissociation of water

$$H_2O = H_2 + \frac{1}{2}O_2 \quad \Delta G^0 = 2.46\text{eV}; \Delta E^0 = 1.23\text{V}$$

In this reaction the reactant molecule is both oxidized and reduced to produce both hydrogen and oxygen.

We have chosen to investigate those surface reactions where light is used to excite the solid near the surface. By using band gap radiation, light can efficiently be converted to excited electron-hole pairs at semiconductor surfaces that may be trapped by the adsorbed molecules before their recombination could occur. The photographic process is a good example of such a surface reaction where the photoexcited mobile charge carriers cause decomposition of the solid in the near surface region. After charge capture, leading to oxidation and reduction that produces silver and halogen
atoms, a diffusion controlled aggregation of silver atoms and the removal of the halogen molecules leads to irreversible photo-decomposition. In our case however, we attempt to transfer charges to and carry out reactions of adsorbed molecules instead of atoms in the solid surface.

Another reaction that is more complex than the water dissociation is the one between gaseous H$_2$O and CO$_2$

\[
\text{CO}_2 + 2\text{H}_2\text{O} = \text{CH}_4 + 2\text{O}_2 \quad \Delta G^\circ = 8.30 \text{ ev mole} ; \Delta \varepsilon^\circ = 1.04 \text{ ev electron}
\]

\[
\text{CO}_2 + 2\text{H}_2\text{O} = \text{CH}_3\text{OH} + \frac{3}{2}\text{O}_2 \quad \Delta G^\circ = 7.15 \text{ ev mole} ; \Delta \varepsilon^\circ = 1.19 \text{ ev electron}
\]

\[
\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO} + \text{O}_2 \quad \Delta G^\circ = 5.32 \text{ ev mole} ; \Delta \varepsilon^\circ = 1.33 \text{ ev electron}
\]

\[
\text{CO}_2 + \text{H}_2\text{O} = \text{HCOOH} + \frac{1}{2}\text{O}_2 \quad \Delta G^\circ = 2.98 \text{ ev mole} ; \Delta \varepsilon^\circ = 1.49 \text{ ev electron}
\]

There are several different types of organic molecules that may be produced by this photosynthetic process and oxygen is liberated. Although the standard free energies for all of these reactions and the free energies per electron transfer, $\Delta \varepsilon^\circ$, are all positive they are of different magnitude. Unlike photosynthesis that leads to the production of complex high molecular weight carbohydrates, the reactions above lead to the formation of small organic molecules of high vapor pressure. Since all of the reactants and products are gaseous, these reactions may be readily investigated at the solid-vapor interface.

Much of the research that is concerned with thermodynamically uphill photochemical reactions has concentrated on photosynthesis in the past, its oxidation and reduction cycles and the elementary charge transfer steps. Only recently has photoelectrochemistry provided a new direction for the investigations of
positive free energy processes.

Surprisingly very little effort has been made to study photonassisted processes that produce small molecules at the solid-vapor interface. There are major advantages in carrying and photo-reactions using gaseous reactants and products as compared to studies at the solid-liquid interface. The surface composition and its changes can be analyzed readily by the modern surface diagnostic-techniques of surface science that require high vacuum. Thus the reaction mechanisms can be studied more easily. The chemical dissolution of the active surface and the absorption of the incident light by the electrolyte are absent. Moreover, the diffusion of reactants and products to and from the surface is more rapid, perhaps an important consideration effecting the rate of the photochemical reaction.

Unlike in photoelectrochemical reactions at the solid-liquid interface however, one cannot apply a variable external potential to facilitate chemical reactions at the solid-gas interface. Recently, there have been successful attempts to dissociate water in an electro-chemical cell by using only light instead of an external potential. Oxygen evolves at the oxide (SrTiO₃, TiO₂) anode and hydrogen at the cathode (Pt or p-type GaP) from a basic aqueous electrolyte using band gap radiation (~3 eV) to illuminate the anode surface. In fact, hydrogen and oxygen evolve at the aqueous electrolyte-solid interface even when the anode and cathode are short circuited, i.e., touching each other.

The success of the photoelectrochemical dissociation of water without the use of an external potential indicated the
intriguing possibility of carrying out photochemical surface reactions with gaseous reactants. The production of hydrogen and oxygen with both separated, and touching oxide (anode) - metal (cathode) surfaces show that there may be several mechanisms of the same photochemical reaction. In explaining the operation of the photoelectrochemical cell, the importance of a Schottky barrier that forms at the oxide-electrolyte interface is invoked. Since photodissociation of water occurs at the surface when platinum and SrTiO$_3$ crystallites are mixed and pressed into a pellet, i.e., in a short-circuit configuration charge transfer at the metal-semiconductor interfaces may also cause sufficient charge separation and the formation of a space charge barrier at the oxide surface to induce water photo-dissociation. Thus, the electrolyte may not be necessary as an active electrical circuit component in this circumstance, when the oxide semiconductor and the metal are touching.

Nevertheless, using water vapor as a reactant instead of an aqueous electrolyte solution is a major departure from the experimental conditions employed in photoelectrochemistry. While large concentrations of OH$^-$ ions are present in the basic solution the water molecules adsorbing on the oxide surface from the gas phase must be dissociated; an added reaction step that is required for the success of the photochemical process. In addition, certain reaction intermediates may be stabilized in solution that would not be stable in the vapor phase.

We have embarked on a program to investigate the adsorption characteristics of CO$_2$, H$_2$O, CO and O$_2$ on SrTiO$_3$ and TiO$_2$ single
crystal surfaces by a combination of techniques that include electron loss spectroscopy (ELS), ultraviolet photoelectron spectroscopy (UPS), auger electron spectroscopy (AES) and low energy electron diffraction (LEED). Simultaneously we have investigated the surface chemical reactions of gaseous CO$_2$ and H$_2$O at the surfaces of an oxide-metal sandwich, SrTiO$_3$ – Pt. This was carried on in a 30 torr ambient pressure of the reactants at 300 K while illuminating the oxide by band gap (>3 eV) radiation from a filtered mercury lamp. We have utilized a small surface area (~1 cm$^2$) single crystal oxide sample that was cleaned and well-characterized by auger electron spectroscopy (AES) before and after the experiments. The use of well-characterized single crystal surfaces instead of the use of higher surface area powders was deemed necessary because of the possible side reactions due to contaminants, mainly carbon. The formation of CH$_4$ by the nearly thermoneutral reaction 2C + 2H$_2$O + CH$_4$ + CO$_2$, $\Delta G^o$ = +2.87 Kcal/mole has been reported. While large surface area powders or polycrystalline deposits are always carbon contaminated, the small area high purity single crystal sample is readily cleaned by a combination of ion bombardments and chemical treatments before the experiments, thus eliminating the possibility of uncontrolled side reactions. However, as a result of the small surface area of our samples it is more difficult to obtain products in detectable concentrations. The photon assisted reaction is carried out at near atmospheric pressure in a specially constructed isolation cell that is located in the center of an ultra-high vacuum chamber. When the cell is open the sample could be cleaned in situ.
by ion bombardment or by chemical treatments at low pressures and the surface composition analyzed by AES. The cell is closed around the sample, then it is pressurized by the introduction of the reactants (CO₂ and H₂O) and the chemical reaction is carried out at any desired surface temperature while the sample is illuminated through a sapphire window.

Using this experimental configuration we have found evidence for the production of methane from gaseous CO₂ and H₂O at the surfaces of SrTiO₃-Pt sandwich. To verify the elementary steps of the complex photoreaction the chemisorption studies will be described at first. Then the photochemical reactions of CO₂ and H₂O will be discussed along with the "blank" experiments that were carried out to identify the photochemically active system.

**Experimental**

A. Equipment

All of the chemisorption experiments were performed in a stainless steel ultra high vacuum (UHV) chamber evacuated by ion and water-cooled titanium sublimation pumps. The base pressure in the system was in the low 10⁻¹⁰ torr range.

A double pass cylindrical mirror analyzer (CMA) with a coaxial electron gun was used as the primary electron source and electron energy analyzer by which electrons emitted into a conical segment with half angle of 42.3° from the axis of the analyzer were collected. In all Auger electron analysis, the CMA was operated at a constant resolution of 1.5 eV. In this way we could resolve detailed structures of the peaks in the \( \frac{dN}{dE} \) Auger spectra,
and give reliable estimates of strontium to oxygen and oxygen to titanium ratios under different conditions of surface preparation.

A primary electron beam with energies between 60-180 eV was used in the electron energy loss experiments. The electron energy loss spectra (ELS) were obtained either by directly measuring the electron energy distribution N(E) as a function of energy loss or its second derivative \(- \frac{d^2N}{dE^2}\). Both methods yielded the same loss peaks except the features in the ELS \(- \frac{d^2N}{dE^2}\) spectra were enhanced. The CMA was operated in the retarded mode with pass energy at 50 eV. However, since the primary electron beam was not energy analyzed, the ultimate resolution was limited by the thermal energy spread of the incident electrons which was about 0.5 eV. The energy positions of the loss peaks were independent of incident electron energies in the range of 60-180 eV. All energy loss spectra reported in this paper were obtained with incident energies \(- 100\) eV. The features of these spectra were very surface-sensitive.

In the UPS studies, the cold cathode discharge lamp was operated to generate the HeI spectral line at 21.2 eV. A two-stage differential pumping manifold was employed to minimize the helium leak flow from the discharge lamp into the ultra-high vacuum chamber which maintained a pressure of \(1-2 \times 10^{-9}\) torr during all UPS experiments. The mass spectrometer indicated that the pressure rise was due to the increase of helium partial pressure in the chamber. The specimen was positioned with its surface normal coincident with the axis of CMA. The angle of incidence of the photons on the specimen was 75° from the normal. The analyser was operated with a constant resolution of 0.035 eV. Typically a spectrum could be
B. Sample Preparation and Experimental Procedure

For the chemisorption studies the specimen used was a 99.99% undoped strontium titanate single crystal with perovskite structure. Samples of (111) orientation, as determined by the Laue back reflection technique, were cut from this crystal and mechanically polished using 0.05 μm Al₂O₃ powders. The specimen was then rinsed in distilled water and mounted on a high density alumina holder, which had a tungsten heater wire located at the back of the sample to allow radiative heating of the crystal. A LEED optics made by Physical Electronics was used to study the surface structure after annealing. Two samples of (111) orientation have been prepared and both gave essentially the same results.

For argon ion bombardment of strontium titanate surfaces, the vacuum chamber was back-filled with argon to a pressure of 6x10⁻⁵ torr. With an accelerating voltage of 2 KeV, the ion bombardment could typically deliver an argon ion beam of 20 μA to the sample surface.

For the photochemical reaction studies the SrTiO₃ crystal samples (1 cm diameter and 1 mm thick disks) were mounted on a disk of 0.001 inch thick Pt foil and were held in place by two straps of Pt foil (1 mm wide) that were spot welded to the Pt foil backing (Figure 2). Although the oxide-metal contact was secure, it was only a relatively poor mechanical electrical contact. The oxide-metal sandwich so prepared was mounted in the UHV chamber. After cleaning by ion bombardment and annealing by
heating in vacuum or in oxygen, an auger spectrum was taken to determine the surface composition. At this point the isolation cell was closed and pressurized with the reactant gases. The CO₂ was Matheson Research Grade and was used without further purification. It contained a small methane impurity which was negligible compared to the methane produced. The pure water was obtained from Scientific Products and was used after several cycles of outgassing by freezing with liquid nitrogen while pumping on the sample. No impurities were detectable in the water by gas chromatography, or mass spectroscopy.

Band gap radiation was provided by a 500 watt high pressure mercury lamp in a water cooled housing. Light from the lamp was collimated and focussed on the sample with two quartz lenses. An infrared filter consisting of a quartz cell filled with NiSO₄ solution was placed between the mercury lamp and the reaction cell, to absorb the heat and transmit the near U.V. With this arrangement we were able to obtain a photon flux of \( \approx 10^{17} \) photons/sec on the 1 cm² crystal surface.

In order to obtain quantitative determination of the reaction product concentration, the gas chromatograph was calibrated using pure methane.

Results

A. Selected Properties of the Clean SrTiO₃ Crystal Surface

Determined from AES, UPS, LEED and ELS Studies.

Stoichiometric SrTiO₃ is an insulator, transparent to visible light (band gap 3 eV). It is cubic (perovskite structure)
t 300°K, but becomes tetragonal at about 110°K. When the 99.99% undoped strontium titanate obtained from the National Lead Company is reduced by heating in a flow of hydrogen at 1000°K for two hours it turns black and exhibits a dark conductivity of \( \sim 1.0 \) (ohm-cm)\(^{-1}\). The AES and UPS Spectra were obtained after ion bombardment at 300°K to remove the impurities (mostly carbon) followed by annealing at 900°K. The AES spectra obtained at 300°K gives peak to peak ratios of \( \frac{\text{Sr}(65\text{eV})}{\text{O}(510\text{eV})} \) and \( \frac{\text{O}(510\text{eV})}{\text{Ti}(380\text{eV})} \) 1.5 and 2.0 respectively for both the stoichiometric and reduced samples. Thus, the surface composition appears to be similar as judged by AES.* It should be noted that the surface composition of \( \text{SrTiO}_3 \) is temperature dependent as shown in a recent study. (6) The (111) crystal face exhibits a (1x1) LEED pattern when ordered. Ordering, however, requires heating to 900°K after ion bombardment. The chemisorption studies were carried out mostly on disordered surfaces due to our inability to anneal the oxide surface at high enough temperature on account of poor thermal contacts. The auger peak to peak ratios were not affected by the different degree of ordering of the (111) surface.

* It appears that the surface composition of the stoichiometric oxide is altered by electron bombardment and it becomes reduced. Thus the similarity of the AES spectra of the stoichiometric and reduced crystals may be due to electron bombardment reduction of the stoichiometric crystal during the time necessary to obtain the spectra.
The UPS spectra were different for the stoichiometric and reduced (111) surfaces of SrTiO$_3$ as shown in Figure 3. Both the stoichiometric and reduced crystals have large concentrations of Ti$^{3+}$ ions. This is different from the results found for TiO$_2$, where the stoichiometric sample has no observable Ti$^3$ concentration.

The transition in the ELS (Figure 4) due to Ti$^{3+}$ in the reduced SrTiO$_3$ sample is significantly broadened, indicating the possibility of band formation. There is an additional transition in the UPS (Figure 3) for the reduced sample near ~11eV indicating differences in the valence band structure.

B. Chemisorption of H$_2$O, O$_2$, CO and CO$_2$ on the SrTiO$_3$(111) Crystal Face in Dark and in Light

When water vapor is introduced into the vacuum chamber at pressures of $10^{-6}$ torr, adsorption on the oxide surface takes place. Typical exposures were about $10^4$ Langmuir. The UPS N(E) spectra in the region of the Ti$^{3+}$ transition are shown in Figure 5. The signal due to the presence of Ti$^{3+}$ ions in the surface decreases upon H$_2$O adsorption indicating that much of the Ti$^{3+}$ is oxidized to Ti$^{4+}$ by the adsorbed water molecule. The work function
is found to increase by 0.4 eV as a result of water adsorption. This may be due to an increase in the band bending near the surface. This in striking contrast to water adsorption on TiO$_2$ which causes a decrease in the work function of 0.8 eV.\(^{(7)}\)

When water adsorption is followed by illumination of the surface with band gap radiation, the Ti$^{3+}$ signal is only partially regenerated as shown in Figure 5. The work function is not affected.

The UPS difference spectra for water adsorption on SrTiO$_3$ (111) (1$\times$1) and a TiO$_2$ surface which was reduced by Ar$^+$ bombardment are shown in Figure 6. The two spectra are quite similar, but they are quite different from that of undissociated water.\(^{(7)}\) Recent calculations by Tsukada, et al, indicate that OH$^-$ may be formed on the reduced TiO$_2$ surface.\(^{(8)}\) From our results it appears the water adsorbs dissociatively on surfaces of TiO$_2$ and SrTiO$_3$ which have significant Ti$^{3+}$ concentrations. Thus, water adsorbs dissociatively on reduced TiO$_2$ and both stoichiometric and reduced SrTiO$_3$. In the process of dissociative adsorption of H$_2$O, the Ti$^{3+}$ sites are oxidized to Ti$^{4+}$.

Oxygen chemisorption on the SrTiO$_3$ (111) crystal face after exposure to $\sim$5x10$^4$L increases the work function by $\Delta \phi = 0.9$ eV. The Ti$^{3+}$ signal is completely removed by chemisorbed oxygen. This is shown in the UPS N(E) spectra that is displayed in Figure 7. Illumination of the surface with bandgap radiation, after O$_2$ adsorption, regenerates a significant amount of Ti$^{3+}$ as shown in Figure 7. However, upon illumination of the O$_2$ covered surface the work function is reduced by only 0.2 eV which is still 0.7 eV greater than the work function of the clean stoichiometric sample. The fact that the work function does not return to the value of
the clean stoichiometric sample upon illumination indicates that not all the adsorbed \( O_2 \) is removed by photodesorption.

Both \( CO \) and \( CO_2 \) give rise to the same UPS difference spectra when adsorbed on the \( SrTiO_3 \) surface. The spectrum is shown in Figure 8. The measurements were taken after exposure of the surface to \( 5 \times 10^4 L \) of these gases. The work function is found to increase by 0.3 eV on adsorption of \( CO_2 \). The \( Ti^{3+} \) signal is significantly decreased. On illumination there is not noticeable change in either the work function or the \( Ti^{3+} \) signal.

Upon heating the sample after \( CO \) adsorption only \( CO_2 \) is observed to desorb, indicating that \( CO \) may be efficiently converted to \( CO_2 \) on the oxide surface.

There is considerable experimental evidence indicating that \( CO \) is readily oxidized to \( CO_2 \) over several transition metal oxide surfaces in addition to \( SrTiO_3 \). (9) An oxygen ion from the crystal lattice is likely to be used for this purpose. The reduction of \( CO_2 \) to \( CO \) that is commonly observed on many transition metal surfaces does not appear to occur on the oxide surface. Another reaction that converts \( CO \) to \( CO_2 \) is its disproportionation \( 2CO \rightarrow C + CO_2 \) that may also occur. We cannot rule out this reaction as a possible path to convert \( CO \) to \( CO_2 \), although we do not see the accumulation of much carbon on the oxide surface. Under reaction conditions carbon is never found to accumulate on the reduced \( SrTiO_3 \) that presents an oxygen deficient surface to the incoming reactants.

Work on photodesorption from oxide surfaces indicate that \( CO_2 \) is the primary species observed as opposed to \( CO \). (14,15) This combined evidence leads us to the conclusion that conversion of
CO$_2$ to CO is not involved in the mechanism of methane formation.

In summary, H$_2$O dissociates at least partly on adsorption as indicated by the electron spectra and oxidizes Ti$^{3+}$ to Ti$^{4+}$ in the process. Ti$^{3+}$ is only partly regenerated by bandgap radiation. Oxygen adsorbs in several states on the surface. It desorbs from the state that is associated with the oxidation of Ti$^3$ to Ti$^4$ and the Ti$^{3+}$ sites are regenerated. Other types of chemisorbed oxygen remain on the surface during illumination, as indicated by the work function change. CO and CO$_2$ give rise to the same changes in the electron spectra indicating that they form the same surface species on the oxide surface. It appears that CO is converted to CO$_2$ by a slow surface reaction.

C. Chemisorption of H$_2$O, O$_2$, CO and CO$_2$ on Pt Surfaces

Water is known to chemisorb only poorly on Pt surfaces at low pressures. It remains molecular on the surface and is bound only weakly. Evacuation of the reaction chamber after exposure of the Pt to high pressures (several torr) of water resulted in total removal of the water at room temperature, clearly indicating weak binding. There was no evidence for water dissociation on the Pt surface even at these higher pressures.

Oxygen chemisorbs on Pt single crystal and polycrystalline foil surfaces at low and high pressures. There is evidence for the presence of chemisorbed oxygen as well as the formation of oxide under appropriate experimental conditions. Under conditions of the photochemical reaction studied here, oxygen should mostly be in the chemisorbed state.
Chemisorbed oxygen also interacts strongly with carbon or adsorbed CO on the Pt surface. The kinetics of oxidation of C or CO on Pt have been studied extensively.\(^\text{11}\)

CO chemisorbs on Pt with a sticking probability of unity even at very low pressures (\(\approx 10^{-9}\) torr). It stays molecular but strongly bound on the metal and it exhibits many binding states with distinguishable heats of adsorption that vary from 32 to 14 Kcal/mole.\(^\text{12}\) Only surface kink sites will dissociate CO to carbon and oxygen on Pt as indicated by photoelectron spectroscopy studies.\(^\text{13}\) Since the concentration of kink sites is a small fraction of the total number of surface sites, most of the CO adsorbed on the Pt surface should remain molecular.

CO\(_2\) adsorbs poorly with a low sticking probability on Pt at low pressures (\(\approx 10^{-6}\) torr). At pressures of several torr that are utilized in our photochemical studies, CO\(_2\) adsorbs as indicated by subsequent thermal desorption. Only CO\(_2\) is observed in our thermal desorption experiments. No carbon buildup on the Pt is observed by AES after exposure to 15 torr CO\(_2\) in the dark. Thus it appears that CO\(_2\) remains largely molecular on the Pt surface in the absence of hydrogen and light and is weakly bound. We find no evidence for the dissociation of CO\(_2\) to CO and O.

D. The Photochemical Reaction of Gaseous H\(_2\)O and CO\(_2\) to Produce CH\(_4\) Over SrTiO\(_3\)-Pt Sandwiches

The reduced oxide SrTiO\(_3\)-Pt sandwich, after cleaning by ion bombardment and heat treatments, is analyzed by AES then enclosed in the isolation cell. The cell is filled with 15 torr H\(_2\)O and 15 torr CO\(_2\). The gas composition is analyzed by the gas chromatograph
and then the experiment commences. The oxide side of the sandwich is illuminated by light of band gap or larger energy using a 500 watt Hg lamp. A NiSO₄ filter is used to screen out the infrared radiation to avoid heating the sample. The thermocouple that is attached to the sandwich registers less than 10° temperature rise throughout the experiments at 300°K.

Methane gas is produced for the first 10 minutes of the illumination and is readily detected by the chromatograph. The number of methane molecules formed is plotted as a function of time in Figure 9. The initial rate of formation is 2x10¹⁴ molecules/min., which corresponds to a quantum yield of 1 molecule of methane per 10⁴ photons. The total amount of methane formed is ~10⁻⁹ moles, that corresponds to about 1 monolayer. The production of methane slows down with time and then stops after 10 minutes. This reaction inhibition is due to a tenacious "poison" since pumping out the reactants and reintroducing fresh H₂O and CO₂ does not regenerate the chemical activity of the surfaces. The photochemical activity is regenerated, however, by renewed ion bombardment and annealing, i.e., complete cleaning of the metal and oxide surfaces. AES indicates the buildup of a monolayer of carbon on the Pt.

There is a thermal generation of methane when a reduced SrTiO₃ sample is used in the oxide-metal sandwich. Upon heating to 600°K in the dark, a monolayer of CH₄ can be generated just as in light at 300°K. In both cases CH₄ production stops after the formation of about a monolayer. It appears that the poisoning reaction is the same in the light-driven and thermally-driven reactions, and we detect a monolayer deposit of carbon on the Pt in both cases. Substitution of CO for CO₂ in the reaction mixture does not increase the methane yield. This observation combined
with the evidence favoring CO\textsubscript{2} in the CO/CO\textsubscript{2} equilibrium over oxides seems to rule out CO as an important intermediate in the reaction paths of methane formation.

The following experiments were carried out to prove that CH\textsubscript{4} productions was indeed the property of the metal-oxide contact. The following experiments all produced no detectable amount of CH\textsubscript{4}:

1. The SrTiO\textsubscript{3}-Pt sample with only CO\textsubscript{2} (no H\textsubscript{2}O) in the presence of light and by heating the sample to 450\textdegree K.

2. The SrTiO\textsubscript{3} crystal without the Pt foil using CO\textsubscript{2} and H\textsubscript{2}O mixtures and illumination.

3. The Pt foil alone using CO\textsubscript{2} and H\textsubscript{2}O mixtures, both with illumination, and by heating the Pt foil to 450\textdegree K.

4. The SrTiO\textsubscript{3}-Pt sample in a CO\textsubscript{2} and H\textsubscript{2}O mixture using illumination with light of energy less than the band gap of SrTiO\textsubscript{3} (light with energy less than the band gap was obtained by placing a Corning glass filter between the NiSO\textsubscript{4} solution filter and the reaction cell).

The last experiment indicates that band gap radiation is necessary for the photoassisted production of CH\textsubscript{4} from CO\textsubscript{2} and H\textsubscript{2}O. This is consistent with the observed necessity for band gap radiation to dissociate H\textsubscript{2}O in the electrochemical cell experiments. These experiments do establish that the photon assisted reaction is a property of the reduced oxide-metal contact system.

Discussion

There are several important observations that help us to understand the photon assisted process leading to the formation of CH\textsubscript{4}.
from CO$_2$ and H$_2$O.

1. Both the oxide SrTiO$_3$ and the metal are needed to observe the production of methane.

2. The photochemical reaction poisons in 10 minutes at 300°K in the reactant mixture. Surface analysis indicates carbon deposition at the Pt surface. While reduced oxide surface remains free of carbon a thermal reaction exists which also produces CH$_4$.

3. Water adsorbs dissociatively on the oxide surface while it remains molecular on the Pt surface. CO is oxidized to CO$_2$ on the oxide surface. O$_2$ chemisorbs on both oxide and metal surfaces. Part of the chemisorbed oxygen that is utilized for the oxidation of Ti$^{3+}$ ions to Ti$^{3+}$ photodesorbs and the Ti$^{3+}$ sites are regenerated.

4. Band gap radiation is necessary to carry out the photochemical reaction.

5. The energy needed to carry out the production of methane from CO$_2$ and H$_2$O is much larger than the band gap of SrTiO$_3$ indicating that the process must occur in a stepwise manner.

The presence of the metal, Pt in our case, appears to be necessary for both catalytic and electrical reasons. Separation of the photon-generated electrons and holes at the oxide surface is likely to be enhanced by the metal-oxide contact. Platinum appears to participate in the CO$_2$ reduction process, as indicated by the carbon deposition on the metal surface, most likely through
its hydrogenation of the molecule or the reaction intermediates.

While the chemisorption studies indicate that $H_2O$ dissociates on the oxide surface, there is little information at this point on the mechanism of $CO_2$ reduction. Since carbon accumulates at the metal surface it appears that at least part of the carbon cycle involved in the reduction of $CO_2$ to $CH_4$ takes place at the metal surface. One possible reduction scheme would be the conversion of $CO_2$ to $CO$ and then into dissociated oxygen and carbon. The rehydrogenation of $C$ to $CH_4$ that is obtained by the dissociation of $CO$ on Ni, Fe and Rh surfaces appears to be an important mechanism for methanation from $CO$ and $H_2$ on these transition metal surfaces. Pt, however, dissociates $CO$ only at kink sites that are present in low surface concentrations, and this process is not likely to account for the formation of the carbon monolayer. Moreover, when $CO$ was substituted for $CO_2$ the photochemical reaction was not enhanced and there is evidence for the oxidation of $CO$ to $CO_2$ at the $SrTiO_3$ surface. Thus we are tempted to rule out this reduction scheme.

A more likely reaction path leading to $CH_4$ formation may be the hydrogenation of $CO_2$ to formic acid ($HCOOH$) or formaldehyde ($H_2CO$) with further reduction to $CH_4$. Future studies will be directed toward verifying the reaction intermediates -- the carbon cycle leading to $CH_4$ production.

We may suggest a tentative reaction sequence leading to the formation of $CH_4$ from $CO_2$ and $H_2O$ on the oxide-metal sandwich.
Water adsorbs dissociatively on the SrTiO$_3$ surface. The photoelectrons and holes produce H atoms (or H$^+$ ions) and O$_2$ molecules.

\[
\text{Ti}^{3+} + \text{H}_2\text{O} = \text{Ti}^{4+} + \text{OH}^- + \text{H} (\text{H}_2)
\]

\[
\text{Ti}^{4+} + 2\text{OH}^- + \text{hv} = \text{Ti}^{3+} + \frac{3}{2}\text{O}_2 + \text{H}_2\text{O}
\]

While O$_2$ photodesorbs, at least in part (there is evidence from our UPS studies that not all of the chemisorbed oxygen is removed by photodesorption) the H atoms or H$^+$ ions migrate onto the Pt surface where the hydrogenation of CO$_2$ and subsequently that of the reaction intermediates occur. It should also be noted that based on the presently available experimental evidence we cannot rule out the possibility of both oxidation and reduction reactions occurring at the oxide surface.

It is notable that CH$_4$ may be produced in the dark over reduced SrTiO$_3$ metal sandwiches. Since the poisoning mechanism seems to be the same as during the photon assisted process, further investigations may permit the steady state production of methane in this circumstance as well. Under certain conditions it can be advantageous to carry out this reaction in the thermal mode instead of under illumination. An added problem of course is the need to stabilize the nonstoichiometric composition in the near surface region. Our UPS studies revealed the likely presence of a Ti$^{3+}$ impurity band that appears to be the cause of the thermally generated electrons and holes that provide the driving force for this thermodynamically uphill reaction.

Perhaps the main difference in carrying out the photochemical surface reaction with adsorbed water vapor as compared
to a basic aqueous solution is the necessity for dissociative adsorption. Hydroxyl ions that are already present in large concentration in the electrolyte have to be produced first when water vapor adsorbs. It would be of importance to compare the rate of water dissociation at the solid-gas and solid-liquid interfaces using the same experimental geometry to evaluate this effect. At present we are tempted to view the photochemical process leading to the formation of methane as consisting of two parts: 1) water dissociation to oxygen and hydrogen and 2) the catalytic reduction of CO$_2$ by the hydrogen. Although the first part yields perhaps the same net reaction as the photoelectrochemical process its mechanism may be entirely different. Both oxidation and reduction may occur on the same oxide surface similar to that in the photographic process. The second process is similar to a methanation reaction: CO$_2$ + 4H$_2$ = CH$_4$ + 2H$_2$O $\Delta G^\circ = -1.4$eV and is thermodynamically allowed. Its mechanism of course may be very complex, consisting of several steps.

There are many future experiments necessary to verify the mechanism of this photosynthetic reaction over the oxide-metal contacts. The role of the metal, electronic or catalytic, should be verified. The effect should be tested using other oxides and other metals as the photochemistry may be markedly changed in this way.

It is likely that other molecules, in addition to methane may also be produced using other appropriate oxide-metal contacts, light of suitable wavelength and gas mixtures of CO$_2$, H$_2$O and N$_2$. Indeed, light assisted reactions over oxide-metal contacts may provide a new route for the production of many different small
Since the formation of CH$_4$ from CO$_2$ and H$_2$O is obviously a multistep process, semiconductors with smaller band gaps should not be ruled out as photoassistant agents in these types of reactions.

**Acknowledgment**

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References

Figure Captions

Fig. 1  Schematic of ultra high vacuum surface analysis chamber equipped with reaction cell.

Fig. 2  Schematic of the SrTiO$_3$(111)-Pt foil sample.

Fig. 3  AES and UPS spectra of stoichiometric and reduced SrTiO$_3$.

Fig. 4  ELS spectra in the region of the Ti$^{3+}$ transition for stoichiometric and reduced SrTiO$_3$.

Fig. 5  UPS N(E) spectra in the region of the Ti$^{3+}$ transition for H$_2$O adsorbed on SrTiO$_3$, before and after illumination.

Fig. 6  UPS difference spectra for H$_2$O adsorbed on TiO$_2$ reduced by Ar$^+$ bombardment and on stoichiometric SrTiO$_3$.

Fig. 7  UPS N(E) spectra in the region of the Ti$^{3+}$ transition for O$_2$ adsorbed on SrTiO$_3$, before and after illumination.

Fig. 8  UPS difference spectra for CO$_2$ and CO adsorbed on stoichiometric SrTiO$_3$.

Fig. 9  Methane production as a function of time of illumination of the SrTiO$_3$-Pt sandwhich in the presence of CO$_2$ and H$_2$O.
Table I: The standard free energies, $\Delta G^\circ$, and the free energy changes per electron, $\Delta \mu^\circ$, for the reduction of CO$_2$ by water to produce a variety of hydrocarbons.
SrTiO$_3$ (III) surface after Ar ion bombardment at $T=27^\circ$C

\[ \frac{\text{Sr}(65\text{ eV})}{0(510\text{ eV})} = 2.8 \]
\[ \frac{0(510\text{ eV})}{\text{Ti}(380\text{ eV})} = 2.2 \]

SrTiO$_3$ (III) surface after reduction in H$_2$ and Ar ion bombardment

\[ \frac{\text{Sr}(65\text{ eV})}{0(510\text{ eV})} = 2.0 \]
\[ \frac{0(510\text{ eV})}{\text{Ti}(380\text{ eV})} = 2.2 \]

SrTiO$_3$ (III) surface after Ar ion sputtering at $27^\circ$C

$T = 27^\circ$C

\[ -10.8 \quad -6.0 \quad -0.6 \]

SrTiO$_3$ (III) surface after reduction in H$_2$ and Ar ion bombardment

\[ -10.8 \quad -6.0 \]

Electron Binding Energy (eV)
ELS for:

(a) Stoichiometric SrTiO$_3$ surface after Ar ion bombardment

(b) Hydrogen-reduced SrTiO$_3$ surface after Ar ion bombardment

Energy Loss (eV)
UPS Spectra at 27°C for:
(a) Clean SrTiO₃ (III)-(1x1) surface
\[ \phi = 4.0 \text{ eV} \]
\[ \Delta \phi = -0.6 \text{ eV} \]

(b) SrTiO₃ (III)-(1x1)+5×10⁴ L H₂O surface
\[ \phi = 4.4 \text{ eV} \]
\[ \Delta \phi = +0.4 \text{ eV} \]

(c) After 10³ sec UV Illumination on the SrTiO₃ (III)-(1x1)+5×10⁴ L H₂O surface
\[ \phi = 4.4 \text{ eV} \]
\[ \Delta \phi = +0.4 \text{ eV} \]
Ar sputtered TiO$_2$(100) + $10^5$ LH$_2$O

Electron Binding Energy (eV): $E_F = 0$

$\Delta N(E)$

$\Delta N(E)$

$\frac{O}{Ti} = 1.3$

$\Delta \phi = +0.4$ eV

XBL786-5298
UPS Spectra at 27°C for:

(a) Clean SrTiO$_3$ (III)-(1×1) surface

-0.6 eV

(b) SrTiO$_3$ (III)-(1×1) + 5×10$^4$ L O$_2$ surface

(c) After 10$^3$ sec. UV Illumination on the SrTiO$_3$ (III)-(1×1) + 5×10$^4$ L O$_2$ surface

Electron Binding Energy (eV)
UPS for SrTiO$_3$ (III)-(lxl) + 5x10$^4$ CO
$\Delta \phi = +0.5$ eV

UPS for SrTiO$_3$ (III)-(lxl) + 5x10$^4$ CO$_2$
$\Delta \phi = +0.4$ eV
$P_{H_2O} = 17$ torr
$P_{CO_2} = 15$ torr

Initial Rate $\sim 2 \times 10^{14}$ molecules/minute
<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta G^\circ ) (eV/mole)</th>
<th>( \Delta E^\circ ) (eV/electron)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( CO_2 + 2H_2O ) = ( CH_4 + 2O_2 )</td>
<td>8.30</td>
<td>1.04</td>
</tr>
<tr>
<td>( CO_2 + 2H_2O ) = ( CH_3OH + \frac{3}{2} O_2 )</td>
<td>7.15</td>
<td>1.19</td>
</tr>
<tr>
<td>( CO_2 + H_2O ) = ( H_2CO + O_2 )</td>
<td>5.32</td>
<td>1.33</td>
</tr>
<tr>
<td>( CO_2 + H_2O ) = ( HCOOH + \frac{1}{2} O_2 )</td>
<td>2.98</td>
<td>1.49</td>
</tr>
</tbody>
</table>

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